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Structure and Chemistry of Chloro(triphenylmethyl)sulfanes

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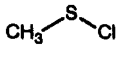
The structures of chloro(triphenylmethyl)mono-, di-, and -trisulfanes were obtained. The monosulfane displayed a triclinic ($P1$) space group, a = 10.792(2) Å, b = 15.090(2) Å, c = 10.027(2) Å, α = 100.15(1)°, β = 103.13(1)°, γ = 88.80(1)°, Z = 4. The disulfane gave a triclinic ($P1$) space group, a = 9.758(1) Å, b = 10.426(2) Å, c = 9.1691(6) Å, α = 97.52(1)°, β = 90.116(1)°, γ = 116.750(1)°, Z = 2. The trisulfane gave an orthorhombic space group ($Pna2_1$), a = 9.224(1) Å, b = 19.196(3) Å, c = 10.308(1) Å, Z = 4. The sulfenyl chlorides decompose above their melting points to mixtures consisting primarily of triphenylchloromethane and sulfur. The sulfur was determined to consist of several allotropes (S_6, S_7, S_8, and S_9). The di- and trisulfanes slowly decompose to the same products at room temperature; the decompositions are enhanced by light. The decomposition of the trisulfane in the presence of dienes gave adducts consistent with the transfer of a two-sulfur species. The disulfane and trisulfane undergo the normal nucleophilic substitution reactions of the monosulfanes.

Introduction

The sulfur–chlorine bond has been the subject of several reviews[1] and possesses a rich and well-studied chemistry.[2] The structures of some chloromonosulfanes (sulfenyl chlorides) are known, but the number is limited. Most of the examples studied are small molecules; the geometry of sulfur dichloride (SCl_2) has been determined using microwave spectroscopy[3,4] and electron diffraction.[5] The structure of methanesulfenyl chloride (1) was also determined by microwave spectroscopy,[6–8] while the trichloro[9] (2) and trifluoro[10] (3) derivatives were examined by electron diffraction. This technique has also been used to measure the geometry of benzenesulfenyl chloride (4).[11] The sulfur–chlorine bonds were found to range between 2.006(4) Å for sulfur dichloride and 2.051(6) Å for 4. The C–S–Cl angle ranged from a low of 98.3(15)° for 2 to a high of 103.0(4)° for sulfur dichloride.

The carbon–sulfur bond lengths ranged from 1.764(12) Å in 4 to 1.824(6) Å in 3. There has been one report of the structure of a sulfenyl chloride determined by X-ray analysis;[12] the unusual α-chloro-α-(chlorosulfenyl)-4-nitro-2,5-dimethoxyphenylacetyl chloride (5) showed a sulfur-chlorine bond length of 1.98 Å, a carbon–sulfur bond length of 1.84 Å, and a C–S–Cl angle of 99.42°.



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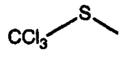

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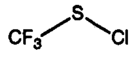

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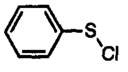

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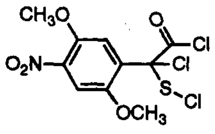

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The chlorodisulfanes have received less attention than the chloromonosulfanes (sulfenyl chlorides), likely as a result of their unavailability in pure form. The structure of disulfur dichloride (S_2Cl_2) was determined in 1969 by electron diffraction[13] and more recently by microwave spectroscopy.[14,15] The sulfur–chlorine bond was longer than that reported for any chloromonosulfane at 2.057(2) Å, and the S–S–Cl angle was also larger (108.2(3)°) than the corresponding C–S–Cl angle.

The structure of chlorotrifluoromethyldisulfane (6) has been studied using vibrational analysis.[16,17] Overall, the chlorodisulfanes exhibit S–S–Cl angles larger than these of the corresponding chloromonosulfanes and exhibit longer sulfur–chlorine bonds.

While the sulfur–chlorine bond has received little structural attention, the sulfur–sulfur bond, especially as disulfanes, has been extensively studied. It is accepted that open-chain nonhindered disulfanes have dihedral angles in the range of 85°, whereas for ring disulfanes the range is from 98.8° for S_8[18] to near 0° for bicyclic disulfanes.[19] The dihedral angles of some hindered disulfanes have been measured. The X-ray crystal struc-

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[1] For example, see: Hardstaff, W. R.; Langler, R. F. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A, Ed.; Marcel Dekker Inc.: New York, 1982; Vol. 4, p 193. Schubart, R. *Organische Schwefelverbindungen*; Houben-Weyl, 1985; E11.

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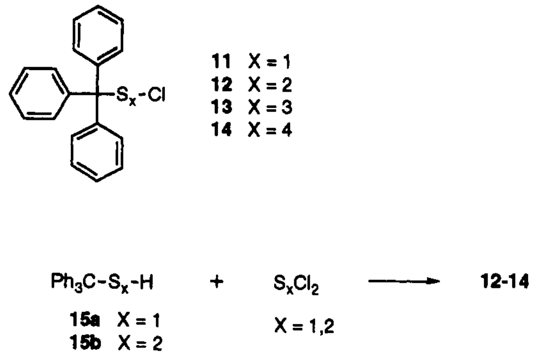
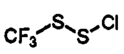
[19] The structure of the bridged bicyclic disulfide 2,3-dithia-8-(*p*-nitrobenzoyl)bicyclo[3.2.1]octane has been determined. The dihedral angle is 1.3°; Folkins, P. L.; Harpp, D. N.; Vincent, B. R. *J. Org. Chem.* **1991**, *56*, 904. For leading references, see: Jørgensen, F. S.; McCabe, P. H. *Tetrahedron Lett.* **1983**, *24*, 319. Snyder, J. P.; Jørgensen, F. S. *Tetrahedron Lett.* **1979**, *35*, 1399. Snyder, J. P.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, *99*, 2931.

0022-3263/94/1959-0806$04.50/0

Scheme I



ture of di-*tert*-adamantyldisulfane[20] (**8**) has been determined, and the dihedral angle is 110.5(9)°; the dihedral angle in bis(triphenylmethyl)disulfane[21] (**9**) was shown to be 110.3°. For di-*tert*-butyldisulfane (**7**), force field calculations (PCMODEL) indicate a dihedral angle as large as 121°. Attempts to prepare the superhindered bis[tris(trimethylsilyl)methyl]disulfane (**10**) were unsuccessful in our hands,[22] although du Mont has recently reported its crystal structure.[21b]



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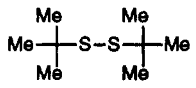

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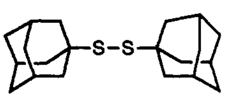

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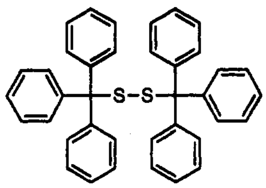

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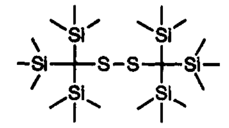

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As part of another program, we have been studying chlorodisulfanes (also known as thiosulfenyl chlorides, sulfenothioyl chlorides, or chlorodisulfanes) as possible diatomic sulfur precursors (S_2). Compounds of this class are known, but their stability appears to be dependent on the presence of strong electron-withdrawing or bulky substituents.[23]

Results and Discussion

Synthesis. Chloro(triphenylmethyl)monosulfane (**11**) was prepared by the direct chlorination of triphenylmethanethiol (**15a**). The higher sulfanes **12** and **13** were obtained by the condensation of **15a** with an excess of SCl_2 and S_2Cl_2, respectively, at low temperature (Scheme I). The thermal instability of the higher members of this class made purification by recrystallization difficult.

Table I. Chemical Data on the Chloro(triphenylmethyl)sulfanes

sulfane	color	mp (°C, dec)	^{13}C NMR (ppm) C-1	C-2	C-3	C-4	C-5
11	light yellow	135–137	72.21	141.76	128.19	129.87	127.90
12	dark orange	91–93.5	77.60	142.17	128.08	130.58	127.65
13	light orange	76–78	74.36	142.60	128.10	130.12	127.48
14	light orange		73.92	142.45	128.12	130.13	127.44

Table II. Selected Bond Lengths and Angles

	monosulfane (11)	disulfane (12)	trisulfane (13)
	Bond Lengths (Å)		
S–Cl	2.018(3)	2.073(2)	2.026(4)
S–S		1.975(2)	2.035(6) 2.011(4)
C–S	1.854(6)	1.912(4)	1.88(1)
C(19)–C(6)	1.511(7)	1.529(6)	1.55(1)
C(19)–C(12)	1.546(8)	1.523(6)	1.53(1)
C(19)–C(18)	1.529(7)	1.538(5)	1.54(1)
	Bond Angles (deg)		
S–S–Cl		108.44(8)	104.7(2)
S–S–S			107.3(2)
C–S–S		111.5(1)	107.9(3)
C–S–Cl	105.2(2)		
C(6)–C(19)–S	113.6(4)	110.6(3)	110.7(6)
C(12)–C(19)–S	109.6(4)	111.0(3)	110.1(6)
C(18)–C(19)–S	97.3(4)	97.5(3)	100.3(5)
S–S dihedral		99.3(2)	-80.2(3) -102.4(3)

Attempts to isolate tetrasulfane **14** in pure form from the condensation of hydro(triphenylmethyl)disulfane[24] (**15b**) and disulfur dichloride at -78 °C were unsuccessful. The ^{13}C NMR spectrum of crude **14** was obtained and consisted of the desired sulfane and the decomposition product triphenylchloromethane; the shifts for **14** could be identified from the spectrum. The physical properties and ^{13}C NMR chemical shifts of **11**–**14** are summarized in Table I.

Crystallographic Analysis. X-ray crystal structures of **11**–**13** were obtained.[25] Compounds **11** and **12** were recrystallized from hexanes; trisulfane **13** was obtained on initial crystallization from ether. The ORTEP[26] drawings of **11**–**13** are included in the supplementary material. Selected bond lengths and angles for **11**–**13** are summarized in Table II. The X-ray crystal structures of **12** and **13** are, to our knowledge, the first reported of a chlorodisulfane and a chlorotrisulfane. On crystallization from ether, sulfane **14** decomposed at -15 °C to yield elemental sulfur.

Monosulfane **11** gave structural data for two independent molecules which were nearly identical. Sulfanes **11** and **12** exhibited no decomposition during X-ray analysis while the crystal of **13** showed extensive decomposition (82%) after 12 h, and therefore, no high-angle data set was obtained; a decay correction was applied to the data. The chosen enantiomorph of **13** gave *R*-factors 0.002 lower than the alternate solution.

The sulfur–chlorine and carbon–sulfur bond distances observed in **11** were in agreement with those measured for

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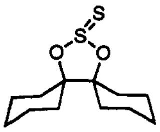
Table III. Molecules with Sulfur–Sulfur Double Bonds

compound	bond length (Å)
$F_2S{=}S$	1.860[29]
$S{=}S{=}O$	1.884[30]
F-S-S-F	1.888[29]
$S{=}S$	1.892[31]
$(RO)_2S{=}S$ 16	1.901[28]
$RN{=}S{=}S$	1.898[32]
$Ph_3NSN{=}S{=}S$	1.908[33]
Cl—S—S—Cl	1.931[13]
disulfide 12	1.975
CS—SC	2.02–2.06[34]

other monosulfanes.[3-12] The observed C–S–Cl angle was also in the range of the structures previously determined.

Disulfane 12 showed surprising structural features. The length of the sulfur–chlorine bond, 2.073(2) Å, is, to our knowledge, the longest reported, while the sulfur–sulfur bond is one of the shortest, with only disulfur dichloride and compounds with known sulfur–sulfur double bonds being shorter. A comparison of bond lengths for compounds with known sulfur–sulfur double bonds is given in Table III; disulfur dichloride is included to demonstrate that the S–S bond length for 12 is intermediate between those of sulfur dichloride and open-chain disulfanes. Some of the chemistry of S_2Cl_2 can be explained by invoking a branch-bonded isomer[27] similar to that observed in S_2F_2. Thionosulfite 16 was the first stable compound with a confirmed thiosulfoxide-like structure.[28]

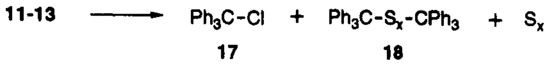


16

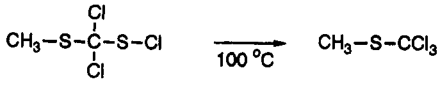
The observed S–S–Cl (108.4°) and C–S–S angles (111.5°) in 12 are two of the largest of their type ever reported. The value of 111° is larger than that found in S_8 (108°) but smaller than the 112.7° for S_2O_2, which is suggested[35] to have double-bond character. The relatively short S–S bond length (1.975Å), coupled with the large sulfur dihedral angle, suggests similar double-bond character for 12 as that found in S_2O_2. The dihedral or torsional angle is larger than that of open-chain disulfanes.

The S–Cl, S–S, and C–S bond lengths found in 13 were consistent with those measured for normal chloromonosulfanes[3-12] and dialkyldisulfanes.[34] The angles, although large, are similar to S_8, indicating that as the chain length increases, the sulfur atoms may adopt an S_8-like geometry. The two dihedral angles about the two S–S bonds differ greatly; the one closer to the triphenylmethyl group C–S–S–S is large (102.4°), and the one adjacent to the chlorine atom S–S–S–Cl is smaller (80.2°). The reason for the difference is not known, but it may also be a result of the hindered rotation of the triphenylmethyl group. A similar effect is observed in organometallic trisulfanes.[36]

Scheme II

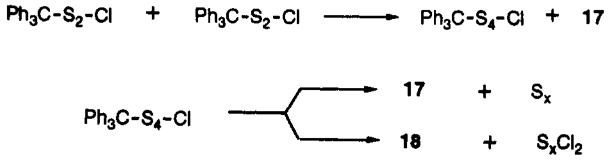


Scheme III



$$CH_3\text{-}S\text{-}CCl_2\text{-}S\text{-}Cl \xrightarrow[100\ ^\circ C]{} CH_3\text{-}S\text{-}CCl_3$$

Scheme IV



Thermal Decomposition of 11–14 as Solids. Sulfanes 11, 12, and 13 are not thermally stable; their stability appears to decrease, as expected, with increasing sulfur content. Each sulfane decomposed when heated at its melting point. Each decomposition sample was analyzed by ^{13}C NMR spectroscopy; 12 and 13 yielded only triphenylchloromethane (17), while 11 displayed a mixture of 17 and the starting material. Sulfur was isolated from all the decomposition mixtures by extraction into chloroform followed by filtration. A similar extrusion was observed by Mott and Barnay on (methylthio)dichloromethanesulfenyl chloride which, when heated to 100 °C, decomposed to give mainly sulfur and methyl(trichloromethyl)sulfane as shown (Scheme II).[37]

After heating 12, HPLC analysis revealed a variety of products. The chromatogram displayed peaks corresponding to 17 and sulfur allotrope S_6, S_7, S_8, and S_9 rings as well as to 10 other products, some of which were identified as bis(triphenylmethyl)sulfanes 18 (Scheme III). Assignments were made by a comparison of the chromatograms of a solution containing S_6–S_{10} rings and a solution of 18, containing 3–12 sulfurs. The S_6:S_8 and S_7:S_8 concentration ratios were determined to be 0.31 and 0.33, respectively, which are much higher than those obtained for liquid sulfur at 120 °C (0.0054 and 0.033, respectively).[38] This indicates that the equilibrium between various sulfur rings observed in liquid sulfur is not found in this decomposition process.

The presence of sulfanes 18, identified in the decomposition carried out in solution (*vide infra*), suggests the following reaction sequence (Scheme IV). The initial step would be the exchange of sulfur atoms to form a chlorosulfane of unknown sulfur content. The chlorosulfane could then decompose with the formation of chloromethane 17 and sulfur or couple to give 18 and a sulfur chloride.

Noticeable decomposition took place with 12 and 13 over a 2-week period. Both compounds exhibit a visible color change after 48 h. Analysis by ^{13}C NMR showed that it was a mixture of the starting sulfane and 17. The decomposition was also enhanced by light as demonstrated in the following experiment. Two samples of 13 were maintained under identical conditions except one was

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stored under ambient light while the second was kept in the dark. The sample exposed to light showed decomposition after only 48 h as visually determined as well as by a comparison of the ^{13}C NMR spectra; the dark sample remained unchanged.

Spectroscopic Analysis. Disulfane 12 gave signals which were anomalous to those of 11 and 13 (Table I). Several of the disulfane carbons are shifted upfield with the effect being most pronounced for the triphenylmethyl carbon. The shift may be attributed to the addition of a second sulfur atom; a similar effect has been observed on the addition of sulfur atoms between alkylmono- and -disulfanes.[39] A third sulfur atom would diminish the steric and electronic interactions between the phenyl rings and the chlorine atom, giving a downfield shift from that found in 12. The rotational restraints of the triphenylmethyl group would also affect the ^{13}C NMR chemical shifts. This effect has been used to explain the unusual shifts observed in the ^1H NMR spectra of hydro(triphenylmethyl)-sulfanes.[40]

It was anticipated that the Raman spectra would give further insight into the molecular structure of the sulfanes. The typical value for the usual S–S symmetrical stretch (Raman) is about 510 cm^{-1}.[41,42] There is reported to be an approximate linear relationship between the frequency of the S–S shift and the dihedral angle.[43] The explanation for this is that as the dihedral angle decreases from 90°, there is a greater $p\pi$–$p\pi$ interaction which destabilizes the S–S bond.[44] This effect has only been observable for compounds with dihedral angles below 60°.

The complex spectrum of 13 may indicate the presence of decomposition products. The breakdown of 12 and 13 has been observed at room temperature and is enhanced by light (*vide supra*); it may decompose in the Raman laser. For example, the signal at 470 cm^{-1} corresponded very well with the signal at 472 cm^{-1} which is the base peak in the Raman spectra of sulfur allotropes S_6 and S_8.[45]

Reaction with Nucleophiles. The reaction of monosulfanes (sulfenyl chlorides) have been studied. Sulfane 11 is well-known and is used extensively as an amine protecting group in amino acid chemistry. Substitution reactions on chloro(pentafluorobenzene)disulfane[46] and chloro(trifluoromethyl)disulfane[47] have been reported. Sulfane 12 reacted with thiols to yield unsymmetrical trisulfanes[48] and has been used as an intermediate in the synthesis of fungal metabolites.[49]

A series of representative reactions were examined as summarized in Schemes V and VI. The sulfanes reacted with carbon nucleophiles to yield mixed sulfanes by displacement of chloride. Reaction with *n*-butyllithium or *n*-butylmagnesium chloride gave the same product, *n*-butyl(triphenylmethyl)sulfanes 21, X = 1–3. The reaction of the Grignard was not as selective with some mixtures being formed. The reaction of *n*-butyllithium gave the butylsulfanes in yields of 36–40%, while *n*-butylmagnesium chloride gave the sulfanes in yields of 46–58%.

Scheme V

$$Ph_3C\text{-}S_x\text{-}Cl \;+\; Bu\text{–}MgCl \longrightarrow Ph_3C\text{-}S_x\text{-}Bu \;+\; MgCl_2$$

$$Ph_3C\text{-}S_x\text{-}Cl \;+\; Bu\text{–}Li \longrightarrow Ph_3C\text{-}S_x\text{-}Bu \;+\; LiCl$$

$$Ph_3C\text{-}S_x\text{-}Cl \;+\; Bu\text{–}SH \longrightarrow Ph_3CS_{(x+1)}Cl \;+\; HCl$$

$$Ph_3C\text{-}Cl \;+\; Bu\text{–}SH \longrightarrow Ph_3C\text{–}S\text{–}Bu \;+\; HCl$$

Scheme VI

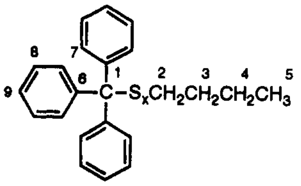
$$Ph_3C\text{-}S_x\text{-}Cl \;+\; Ph_3C\text{–}SH \longrightarrow Ph_3C\text{–}S_{(x+1)}\text{-}CPh_3 \;+\; HCl$$

$$Ph_3C\text{-}S_x\text{-}Cl \;+\; NaSH \longrightarrow Ph_3C\text{–}S_{(x+1)}\text{-}H \;+\; KCl$$

$$Ph_3C\text{-}S_x\text{-}Cl \;+\; Bu\text{–}SH \longrightarrow Ph_3C\text{–}S_{(2x+1)}CPh_3 \;+\; HCl$$

The reaction with thiols gave the unsymmetrical sulfane. The reaction of 11–13 with 1-butanethiol yielded 21 with X = 2–4, respectively. The sulfanes from the reaction of 11 and 12 were identical to those obtained in the reaction of 10 and 11 with the carbon nucleophiles. The sulfanes were isolated in yields of 52–72%. To confirm the structure of butyl(triphenylmethyl)monosulfane (21a), it was independently synthesized by the direct condensation of 1-butanethiol with 17.

$Ph_3C\text{–}H$ **19** $Ph_3C\text{·}OH$ **20**



21a X = 1
21b X = 2
21c X = 3
21d X = 4

The reaction of 12 and 13 with 15a gave bis(triphenylmethyl)trisulfane (18c) and -tetrasulfane (18d) in yields of 88% and 80%, respectively. The identification was made by comparison with the authentic compounds.[21,24] There was no reaction between 11 and 15, presumably due to steric hindrance.

The sulfanes were anticipated to be useful precursors for the synthesis of hydro(triphenylmethyl)sulfanes (15a–d) by a substitution reaction of the chloride with sodium hydrosulfane (NaSH). In no reaction was any hydrosulfane isolated, but the reaction did yield bis(triphenylmethyl)sulfanes 18; the formation was confirmed by a comparison with the independently synthesized compounds. The reaction of 11 produced bis(triphenylmethyl)trisulfane (18c) as the major product; correspondingly, 12 produced bis(triphenylmethyl)pentasulfane (18e), and 13 gave bis(triphenylmethyl)heptasulfane (18f). The products likely result from the reaction of the produced hydrosulfane with the reactant chlorosulfane.

Reaction of 12 and 13 with potassium phthalimide (22) gave the corresponding phthalimido(triphenylmethyl)di- and -trisulfanes (23a and 23b). The identities of the products were confirmed by ^{13}C NMR and by elemental analysis.

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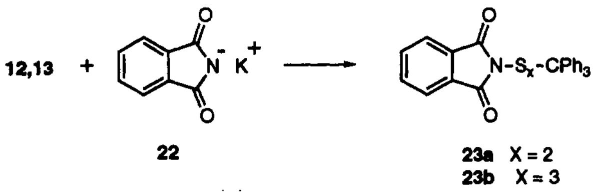
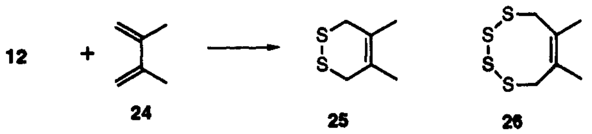
Scheme VII

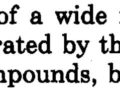


Scheme VIII



Reaction of 11–13 with 1,3-Dienes. Since the initial report of a diatomic sulfur precursor reagent in 1984 by Steliou,[50] several other procedures for the transfer of diatomic sulfur have been discovered.[51] We have recently found[52] that the reaction of 12 with 2,3-dimethyl-1,3-butadiene (24) gave a product consistent with the trapping of a two-sulfur species (1,2-dithia-4,5-dimethyl-4-cyclohexene (25))[51,52] but proceeding by a different mechanism. Also isolated was a second product identified as the cyclic tetrasulfane 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (26).

In earlier experiments,[53] it was postulated that tetrasulfane 26 on reaction with triphenylphosphine would desulfurize to the cyclic trisulfane 27; this was not observed, but instead, only disulfane 25 (and unreacted 26) were identified. Surprisingly, there was no evidence in the ^{1}H NMR spectra for the formation of the cyclic trisulfane. In our laboratory, we have previously had difficulty in the synthesis of cyclic trisulfanes.[53]



27

The reaction of monosulfane 11 with diene 24 for 72 h did not yield either 25 or 26, but a small amount of sulfur was isolated.

The chemistry of 12 and 13 appears to be analogous to that of the corresponding monosulfane. These molecules permit the synthesis of a wide range of organic poly(sulfanes) as demonstrated by the synthesis of a representative series of compounds, butyl(triphenylmethyl)sulfanes 21.

Experimental Section

General Methods. Melting points were measured using a Gallenkamp capillary apparatus and are uncorrected. Products were identified from the ^{13}C and ^{1}H NMR spectra unless otherwise stated. Commercially available compounds were obtained from Aldrich Chemical Co. (Milwaukee, WI). Silica gel chromatography was performed on Merck Kieselgel 60 (230–400 mesh, no. 9385) using flash chromatography.[54] Chromatographic solvents were fractionally distilled prior to use. All reactions were monitored by thin-layer chromatography carried out on 0.25-mm Merck silica gel plates (60F-254), using UV light and a 10% sulfuric acid ethanolic solution of ammonium molybdate–cerium sulfate developing dip. All TLC and column chromatography solvent mixtures are volume percentages. Sulfuryl chloride, sulfur dichloride, and disulfur dichloride were purified by distillation and used immediately. Triphenylmethanethiol (15a) was prepared from triphenylmethanol by known methods.[55]

Preparation of Chloro(triphenylmethyl)monosulfane (11). This was prepared from 15a and sulfuryl chloride was described by Vorländer and Mittag.[56] The UV-visible spectrum for each of 11, 12, and 13 was determined in chloroform; each sulfane exhibited two absorption maxima at 244 and 254 nm.

Preparation of Chloro(triphenylmethyl)disulfane (12). Chloro(triphenylmethyl)sulfane (12) was prepared according to the procedure of Harpp and Ash.[57] To a stirred solution of sulfur dichloride (3.60 g, 35.6 mmol) in 50 mL of anhydrous ether under a nitrogen atmosphere at −78 °C was slowly added a solution of 15a (7.61 g, 26.1 mmol) in 80 mL of anhydrous ether over 1 h. During this period, an orange–yellow precipitate formed in the reaction flask. The mixture was warmed to rt and concentrated to 30 mL under reduced pressure, and the solid was separated by filtration. Crystallization from hexanes gave an orange solid (6.54 g, 73%), mp 91–93.5 °C dec (lit.[57] mp 91–93 °C). Once initial crystallization had occurred, the solution was cooled to −15 °C. Storage of the solution at rt for more than 12 h resulted in decomposition, as evidenced by a brown color. The products of the decomposition were not identified. Caution is required during recrystallization as excessive heating of the hexanes solution results in the formation of a yellow precipitate, identified as sulfur (TLC). 12: ^{1}H NMR (CDCl$_3$) δ 7.34 (m); ^{13}C NMR (CDCl$_3$) δ 77.6 (C–S), 127.7, 128.1, 130.6, 142.2; IR (KBr) cm^{-1} 3048, 3032, 3019, 1486, 1438, 1000, 974, 890, 758, 728, 699, 661, 626, 616, 507, 482; Raman (solid) cm^{-1} 534, 483, 422, 416, 402, 341. Anal. Calcd for $C_{19}H_{15}S_2Cl$: S, 18.69. Found: S, 18.06.

Preparation of Chloro(triphenylmethyl)trisulfane (13). The procedure used was similar to that for the preparation of 12 except disulfur dichloride was substituted for sulfur dichloride. To a stirred solution of disulfur dichloride (2.70 g, 20 mmol) in 50 mL of anhydrous ether at −78 °C under a nitrogen atmosphere was slowly added a solution of 15a (4.1 g, 15 mmol) in 80 mL of anhydrous ether. The reaction mixture was allowed to warm slowly to rt and concentrated to 30 mL under reduced pressure. Crystallization resulted on cooling at −15 °C for 24 h. Filtration yielded a light orange solid (3.4 g, 61%), mp 76–78 °C dec: ^{13}C NMR (CDCl$_3$) δ 74.4 (C–S), 127.5, 128.1, 130.1, 142.6; IR (KBr) cm^{-1} 3056, 3029, 1489, 1440, 1000, 756, 735, 694, 669, 626, 616, 488, 472, 459; Raman (solid) cm^{-1} 519, 487, 470, 454, 449, 357, 346. Anal. Calcd for $C_{19}H_{15}S_3Cl$: C, 60.96; H, 4.01. Found: C, 61.02; H, 4.01.

Preparation of Chloro(triphenylmethyl)tetrasulfane (14). To a stirred solution of disulfur dichloride in 50 mL of ether at −78 °C was slowly added dropwise a solution of hydrosulfane[58] 15b in 50 mL of ether. The solution was stirred, concentrated to 10 mL under reduced pressure, and stored at −15 °C. A yellow precipitate was removed from the solution after 24 h and was identified to be sulfur (TLC), mp 100–114 °C. All attempts to precipitate the tetrasulfane were unsuccessful.

A small aliquot of the original solution was removed and the solvent removed under reduced pressure. The gummy solid was taken up in CDCl$_3$ and a ^{13}C NMR spectrum acquired. The spectrum had signals corresponding to 14 (^{13}C NMR (CDCl$_3$) δ 73.9 (C–S), 127.4, 128.1, 130.1, 142.5) but was contaminated with 17, the decomposition product. The sulfane 14 decomposed in solution as the signals for 17 increased in intensity over the

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spectrum acquisition. A yellow precipitate formed in the NMR solution that was identified as sulfur (TLC).

Crystallographic Analysis. A single crystal of the sulfane was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu Kα radiation at 1.75 kW (λ = 1.54178 Å). The structures were obtained at either 20 or 21 °C using ω–2θ scan type and a scan rate of 32.0°/min. The structures were solved by either direct methods or the patterson method and refined using full-matrix least squares.

Thermal Decomposition of 11, 12, and 13. A sample of the sulfane was heated to its melting temperature and the resulting mixture analyzed by acquiring a ^{13}C NMR spectrum. For 12 and 13 as the heating was maintained above the melting point, a yellow solid developed. Extraction in chloroform followed by filtration yielded elemental sulfur (TLC, mixed melting point).

Room-Temperature Decomposition of Solid 13. Effect of Ambient Light. Two samples of 13 were prepared; one sample was maintained in the dark and the other in ambient light. After 48 h, each sample was dissolved in $CDCl_3$ and a ^{13}C NMR spectrum acquired. The sample in light showed a considerable amount of 17 which was not present in the sample maintained in the dark. The sulfur formed in the decomposition (TLC) was isolated by filtration of the NMR solution.

Reaction of 12 and 13 with *n*-Butylmagnesium Chloride. General Procedure. To a solution of sulfane (1 mmol) in ether at 0 °C under N_2 was added *n*-butylmagnesium chloride (0.5 mL of a 2.0 M solution in ether). The mixture was stirred for 1 h over which time the yellow color of the sulfane solution dissipated. Column chromatography (20% $CHCl_3$ in hexanes) yielded *n*-butyl(triphenylmethyl)sulfanes **21**. The reaction with either di- or trisulfane also yielded small amounts of **18**.

Butyl(triphenylmethyl)disulfane (21b): 0.167 g, 46%; ^{1}H NMR ($CDCl_3$) δ 0.731, 0.766, 0.801 (t, 3H), 1.13–1.34 (m, 4H), 1.64, 1.68, 1.71 (t, 2H), 7.23–7.48 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 21.5 (CH_2), 30.8 (CH_2), 36.4 (CH_2), 70.8 (C–S), 126.8, 127.7, 130.1, 143.9; MS (EI, 70 eV, 30 °C) *m/z* 243 (Ph_3C^+, 100), 165 ($[Ph_2C\text{–}H]^+$, 41), 57 ($[C_4H_9]^+$, 11). A second fraction was isolated which was identified as **18d**.

Butyl(triphenylmethyl)trisulfane (21c): 0.23 g, 58%; ^{1}H NMR ($CDCl_3$) δ 0.821, 0.858, 0.894 (t, 3H), 1.25–1.56 (m, 4H), 2.58, 2.61, 2.65 (t, 2H), 7.17–7.35 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 21.5 (CH_2), 3.10 (CH_2), 39.3 (CH_2), 73.2 (C–S), 127.1, 127.9, 130.4, 143.6. A second impure fraction was obtained which was identified to be a mixture of **21c**, **18c**, and **18d**.

Reaction of 12 with *n*-Butyllithium. To a solution of **12** (0.68 g, 2.0 mmol) in 25 mL of ether at −78 °C under nitrogen was added 0.8 mL of a 2.5 M solution of *n*-butyllithium. The resulting solution was stirred at −78 °C and allowed to warm slowly to rt. The mixture was washed with water and filtered to remove a yellow precipitate (9.1 mg) identified as sulfur (TLC). The mixture was separated, and the ether layer was dried over anhydrous Na_2SO_4 and chromatographed on silica gel with 20% $CHCl_3$ in hexanes to yield a small amount of sulfur (TLC, 4.5 mg) and two other fractions. The second fraction was *n*-butyl(triphenylmethyl)disulfane (**21b**) (0.291 g, 40%) and gave appropriate ^{13}C and ^{1}H NMR spectra. Fraction 3 was a mixture of **18b** and **18c** which on removal of the solvent was a brittle foam.

***n*-Butyl(triphenylmethyl)sulfane (21a).** The reaction of **11** was repeated as above to yield **21a** (0.12 g, 36%): ^{1}H NMR ($CDCl_3$) δ 0.780, 0.809, 0.844 (t, 3H), 1.28–1.42 (m, 4H), 2.14, 2.18, 2.21 (t, 2H), 7.19–7.48 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 22.1 (CH_2), 30.7 (CH_2), 31.7 (CH_2), 66.3 (C–S), 126.5, 126.8, 129.6, 145.1.

Reaction of 11–13 with 1-Butanethiol. General Procedure. To a solution of the sulfane (0.10 mmol) in 25 mL of ether was added 1-butanethiol (0.80 g, 0,10 mmol). The resulting mixture was stirred in the dark for 8 h under N_2. TLC showed a mixture of four components identified as sulfur, 1-butanethiol, **18**, and **21**. Chromatography of the resulting mixture on silica gel with 20% $CHCl_3$ in hexanes yielded the sulfane.

Disulfane (21b): 0.184 g, 52%; spectra were identical to those obtained in the reaction of **12** and *n*-butylmagnesium chloride.

Trisulfane (21c): 0.284 g, 72%; spectra were identical to those obtained in the reaction of **13** and *n*-butylmagnesium chloride.

Tetrasulfane (21d): 0.245 g, 62%; ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 21.5 (CH_2), 31.0 (CH_2), 38.9 (CH_2), 73.5 (C–S), 127.2, 127.9, 130.3, 143.1.

Preparation of 21a. Alternative Procedure. To 50 mL of toluene were added **17** (2.78 g, 0.001 mol) and 1-butanethiol (0.80 g, 0.001 mol), and the mixture was refluxed for 24 h under N_2. The solution was allowed to cool to rt and the solvent removed under reduced pressure. The brown solid (near quantitative) was recrystallized from ethanol, mp 62–64 °C.

Reaction of 11–13 with Triphenylmethanethiol (15a). A mixture of the sulfane (0.10 mmol) and **15a** (0.276 g, 0.10 mmol) in 25 mL of ether was stirred for 24 h in the dark under N_2. The resulting mixtures were analyzed by ^{13}C NMR. The sulfanes were isolated by removal of the solvent followed by drying under vacuum to yield brittle foams. The sulfanes were identified by comparison of the ^{13}C NMR spectra with those of the authentic compounds.[21,24] Reaction of **13** yielded **18d** (0.56 g, 88%), while **12** gave **18c** (0.49 g, 80%). The monosulfane **11** did not react.

Reaction of 11–13 with Anhydrous Sodium Hydrosulfane (NaSH). To each sulfane in 25 mL of ether at 0 °C was added NaSH (2 equiv) as a fine powder. The mixture was stirred under nitrogen for 24 h at ambient temperature. The mixture was filtered and the solvent removed under reduced pressure to give a brittle foam. Chromatography on silica gel with 20% $CHCl_3$ in hexanes gave bis(triphenylmethyl)sulfane **18**. Reaction of **11** (0.310 g, 1 mmol) gave **18c** (0.11 g, 38%). Reaction of **12** (0.342 g, 1 mmol) gave **18e** (0.19 g, 58%). Reaction of **13** (0.187 g, 0.5 mmol) gave **18f** (0.082 g, 46%).

Reaction of 11 with Potassium Phthalimide (22). Preparation of Phthalimido(triphenylmethyl)disulfane (23a). The preparation of **23a** is a modification of the procedure of McClaskey, Kohn, and Moore[59] who prepared other phthalimidodisulfanes. To a solution of **22** (0.93 g, 5 mmol) in 10 mL of water were added 10 g of crushed ice and a solution of **12** (1.71 g, 5 mmol) in 20 mL of hexanes. The reaction mixture was stirred vigorously for 2 h. Within 10 min of mixing, the color of the chlorodisulfane dissipated and a white precipitate formed. The precipitate was isolated by filtration, washed with water, and air-dried to yield a white solid (1.93 g), mp 145–159 °C. Recrystallization from ethanol gave an analytical sample, mp 187–193 °C dec: R_f = 0.51 (chloroform); ^{1}H NMR ($CDCl_3$) δ 7.14–7.18 (m, 9H), 7.32–7.37 (m, 6H), 7.79 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 72.5 (C—S), 123.7, 127.3, 127.8, 130.1, 132.0, 134.5, 143.0, 166.4 (C=O); MS (EI, 70 eV, 205 °C) *m/z* no M^+ 244 (82.2), 243 (Ph_3C^+, 74.7), 166 (Ph_2C^+, 71.7), 165 ($[Ph_2C\text{–}H]^+$, 100), 104 (56.2). Anal. Calcd for $C_{27}H_{19}NO_2S_2$: C, 71.52; H, 4.19; N, 3.90. Found: C, 71.57; H, 4.18; N, 3.00.

Reaction of 13 with 22. Preparation of Phthalimido(triphenylmethyl)trisulfane (23b). To a solution of **13** (0.187 g, 0.5 mmol) in 25 mL of ether was added **22** (0.186 g, 1.0 mmol) as a fine powder. The heterogeneous mixture was stirred for 4 h under N_2 over which time the yellow color of the trisulfane dissipated. The reaction was filtered to remove excess **22** and KCl. TLC with 20% $CHCl_3$/hexanes showed a product and a small amount of **18**. Removal of the solvent under reduced pressure followed by recrystallization gave a white solid (0.11 g, 47%), mp 128–134 °C dec: R_f = 0.64 ($CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.22–7.41 (m, 15H), 7.74–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 73.93 (C—S), 123.97, 127.27, 127.81, 130.29, 132.10, 134.68, 142.74, 166.81 (C=O). Anal. Calcd for $C_{27}H_{19}NO_2S_3$: C, 66.77; H, 3.95; N, 2.88. Found: C, 67.06; H, 4.18; N, 2.79.

Reaction of 11 with 2,3-Dimethyl-1,3-butadiene. To a solution of **11** (0.620 g, 2 mmol) in 25 mL of dry CH_2Cl_2 was added 2,3-dimethyl-1,3-butadiene (0.242 g, 3.0 mmol). The mixture was heated at reflux in the dark for 72 h and then chromatographed on silica gel with 5% $CHCl_3$ in hexanes. A small amount of sulfur was formed. No **25** or **26** was detected in the ^{1}H NMR spectrum of the reaction mixture.

Reaction of 13 with 1,3-Dimethyl-1,3-butadiene. To a solution of **13** (0.187 g, 0.50 mmol) in dry CH_2Cl_2 was added

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2,3-dimethyl-1,3-butadiene (0.121 g, 1.50 mmol). The mixture was heated to reflux in the dark for 2 h and then chromatographed on silica gel with 5% $CHCl_3$ in hexanes to yield 12.6 mg of a 1:3 mixture of **25** (4%) and **26** (9%).

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Supplementary Material Available: ORTEP diagrams for compounds **11**, **12**, and **13** (3 pages). The material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.